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AB - A metallic oxide thin film and a transparent primer layer of high molecular material having Tg of not less than 60[deg]C and Mw 10000-20000 are stacked on one surface of a transparent base of high molecular material.

- ADVANTAGE :

Mechanical strength can be improved without lowering gas barrier property.

ICAI- B32B9/00; B32B9/04; B65D65/00

ICCI- B32B9/00; B32B9/04; B65D65/00

INW - HACHIFUSA K; SASAKI N; SEKIGUCHI M; YOSHIKAWA M

IW - EVAPORATION FILM LAYER MEMBER IMPROVE MECHANICAL STRENGTH GAS BARRIER PROPERTIES DECREASE SURFACE TRANSPARENT BASE METALLIC OXIDE THIN PRIME HIGH MOLECULAR MATERIAL

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NC - 1

NPN - 2

OPD - 1993-09-20

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TI - Evaporation film layered member of improved mechanical strength without gas barrier property decrease - has on surface of transparent base, metallic oxide thin film and transparent primer layer of high molecular material

A01 - [001] 017; P0000

- [002] 017; K9712 K9676; B9999 B5447 B5414 B5403 B5276; ND01; Q9999 Q9369; B9999 B4091-R B3838 B3747; K9574 K9483; K9698 K9676; B9999 B4864 B4853 B4740; K9870 K9847 K9790; B9999 B4397 B4240

A02 - [001] 017; P0000

- [002] 017; Q9999 Q7192 Q7114; K9610 K9483; B9999 B5436 B5414 B5403 B5276; B9999 B5618 B5572; B9999 B5094 B4977 B4740; ND01; Q9999 Q9369; B9999 B4091-R B3838 B3747; K9574 K9483; K9698 K9676; B9999 B4864 B4853 B4740; K9870 K9847 K9790; B9999 B4397 B4240

PATENT ABSTRACTS OF JAPAN

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(54) VAPOR-DEPOSITED FILM LAMINATION

(57)Abstract:

PURPOSE: To provide a vapor-deposited film lamination which is colorless and transparent and has high gas barrier properties not deteriorating against an action such as bending or pulling to be inflicted from outside after processing and a high mechanical strength with superb practical applicability.

CONSTITUTION: A transparent primer layer 3 of a polymer material with excellent size stability and transparency, at a glass transition point of 60°C or higher and further, with a molecular weight of 10000 to 20000, is laminated on a thin film layer 3 with a thickness of 300 to 3000Å consisting of a metal oxide provided on a substrate 2 of transparent polymer material. Consequently, a physical and mechanical stress is absorbed and moderated by the transparent primer layer, so that the lamination shows a high light permeability even after the application of the physical and mechanical stress, and the amount of gas passing through a thin film can be minimized.



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CLAIMS

[Claim(s)]

[Claim 1]A 300-3000-A-thick metal oxide thin film layer is provided in at least one field of a substrate which consists of a polymer material which has transparency, A deposition film layered product which laminates a transparent primer layer which consists of a polymer material which has the transparency which is not less than 60 ** of glass transition points, and has a molecular weight between 10000-20000 on this metal oxide thin film layer, and is characterized by things.

[Claim 2]The deposition film layered product according to claim 1, wherein said metal oxide thin film layers are magnesium oxide, oxidized silicon, and an aluminum oxide.

[Claim 3]The deposition film layered product according to claim 1, wherein said transparent primer layer is polyester resin.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the deposition film layered product which starts the deposition film layered product which forms the vacuum evaporation membrane layer of a metallic oxide, especially has GASUBARIA nature.

[0002]

[Description of the Prior Art] The wrapping used for the package of foodstuffs, drugs, precision electronic components, etc. in recent years, In order to control oxidation of protein, fats and oils, etc., and deterioration in deterioration of contents, especially foodstuffs and to hold the taste and freshness further, In order to control deterioration of an active principle in the drugs for which the handling by an aseptic condition is needed and to maintain efficacy, In order to prevent the corrosion of a metal part, bad insulation, etc. in precision electronic components furthermore, it is necessary to prevent influence with the gas which deteriorates oxygen, the steam, and the other contents which penetrate wrapping, and having the GASUBARIA nature which intercepts these gases (gas) is called for.

[0003] The sake, Polymer Division resin compositions generally said for GASUBARIA nature to be comparatively high, such as polypropylene (KOP), polyethylene terephthalate (KPET) or an ethylene vinyl alcohol copolymer (EVOH) which carried out the coat of the vinylidene chloride resin from the former, are used as a gas barrier material. The metallic foil, the suitable Polymer Division resin composition (if independent) which consist of metal used for wrapping, such as a packaging film and aluminum The packaging film which used for wrapping the metal deposition film which vapor-deposited metal or metallic compounds, such as aluminum, even if it was resin which does not have high GASUBARIA nature has generally been used.

[0004] However, the packaging film which uses only the above-mentioned Polymer Division resin composition, It is ** that it is not only inferior to GASUBARIA nature, but are easy to be influenced by temperature and humidity, and GASUBARIA nature deteriorates further depending on the change compared with the metal deposition film in which the foil using metal or metallic compounds, such as aluminum, and a vacuum evaporation film were formed. On the other hand, although the metal deposition film in which the foil using metal or metallic compounds, such as aluminum, and a vacuum evaporation film were formed had being influenced [little] by temperature, humidity, etc. and was excellent in GASUBARIA nature, it had a fault to which it is supposed that can see through the contents of a packed body and they cannot be checked.

[0005] Then, magnesium oxide which is indicated, for example to the 3442686th JP,S63-28017,B of an United States patent, etc. as a charge of package material which conquered these faults, The film which formed the vacuum evaporation film by means forming, such as a vacuum deposition method and sputtering process, on the high polymer film is developed in metallic oxides, such as oxidized silicon and an aluminum oxide. Having gas cutoff nature, such as transparency and oxygen, and a steam, is known, and this film is made suitable as a charge of package material which has both the transparency and GASUBARIA nature who cannot get with a metal deposition film.

[0006]

[Problem(s) to be Solved by the Invention] However, even if it is a film suitable for the above-mentioned charge of package material, as a container or a packing material, It is hardly used with a deposition film

simple substance, and the deposition film surface is made to complete a packed body for a character, a pattern, etc. through various processes, such as shape working to packed bodies, such as lamination with other substrates, such as a printing process or a film, and a container, as post processing after vacuum evaporation. Therefore, while holding enough transparency and GASUBARIA nature peculiar to a deposition film, when it is necessary to set up the optimal printing conditions for coating printer's ink directly and and performs shape working, for considering it, for example as saccate, it is necessary to apply to a bag sealer.

[0007]Therefore, if the vacuum evaporation side of a deposition film is directly coated with printer's ink, contraction of the printer's ink by desiccation will get across to a vacuum evaporation film, the damage to a crack, a crack, etc. will occur, and if it applies to a bag sealer, the damage to a crack, a crack, etc. will occur on a vacuum evaporation film by cover printing in the Serra part. It has the problem that the high GASUBARIA nature which gases, such as air and a steam, should permeate and it should originally have from this damaged part will fall.

[0008]Namely, only the transparency which can face the contents themselves squarely as conditions used as a packed body, High gas-barrier ** which intercepts the gas etc. which affect it to contents. What has a mechanical strength (or flexibility) to which a function is not reduced to the physical and mechanical stress by processing to a packed body, etc. is called for, and the wrapping which fills these all at present is not found out.

[0009]Then, it aims at providing the high transparent gas barrier material of the practicality which has a mechanical strength to which GASUBARIA nature does not fall to an operation of bending from the outside by post processing, hauling, etc. while this invention has high GASUBARIA nature transparently and colorlessly.

[0010]

[Means for Solving the Problem]This invention is made that an aforementioned problem should be solved and the invention according to claim 1, A 300-3000-Å-thick metal oxide thin film layer is provided in at least one field of a substrate which consists of a polymer material which has transparency, A transparent primer layer which consists of a polymer material which has the transparency which is not less than 60 ** of glass transition points, and has a molecular weight between 10000-20000 on this metal oxide thin film layer is laminated, and it is a deposition film layered product characterized by things.

[0011]An invention indicated to Claim 2 is a deposition film layered product, wherein metal oxide thin film layers are magnesium oxide, oxidized silicon, and an aluminum oxide.

[0012]An invention indicated to Claim 3 is a deposition film layered product, wherein a transparent primer layer is polyester resin.

[0013]

[Function]By laminating the transparent primer layer which consists of a polymer material which has the transparency excellent in dimensional stability on the metal oxide thin film layer provided in the substrate which consists of a polymer material which has transparency according to the deposition film layered product of this invention, Since mechanical stress, such as cover printing of the Serra part in hauling contraction, etc. and bag manufacture at the time of printer's ink desiccation, is absorbed and eased by a transparent primer layer, while a high light transmittance state is shown also after receiving physical and mechanical stress, the gas which penetrates a thin film can be stopped low.

[0014]

[Example]Working example of this invention is described in detail using Drawings. Drawing 1 is a sectional view explaining the deposition film layered product of this invention.

[0015]First, the composition of the deposition film layered product of this invention is explained with reference to drawing 1. 1 is a deposition film layered product of this invention, and the thin film layer 3 which consists of a vacuum evaporation film of a metallic oxide is formed in the surface of the substrate 2. This thin film layer 3 may be formed in both sides of the substrate 2, and may be formed in a multilayer.

[0016]It is a polymer material which has transparency, if the substrate 2 is especially water-white, it is good, and what is used as wrapping is usually preferred. For example, polyester film, such as polyethylene terephthalate (PET) and polyethylenenaphthalate, Polyolefin films, such as polyethylene and polypropylene, polystyrene films, A polyamide film, a polyvinylchloride film, a polycarbonate film, a polyacrylonitrile film, a polyimide film, etc. are used, it is possible for the substrate 2 either extension or to un-extend, and it

has a mechanical strength and dimensional stability. The polyethylenenaphthalate extended arbitrarily is used especially for 2 shaft orientations. These are processed into film state and it is used. Furthermore smooth nature is excellent and a film with little quantity of an additive agent is preferred. In order to improve adhesion of a thin film, corona treatment, low-temperature plasma treatment, and ion bombardment processing may be performed to the surface of this substrate 2 as pretreatment, and a chemical treatment, solvent treatment, etc. may be further performed to it.

[0017]Although, as for the substrate 2, thickness in particular does not receive restriction, if the processability in the case of forming that it is also when laminating the fitness as wrapping and other layers, and the thin film layer 3 is taken into consideration, it is the range of 3-200 micrometers practical, and it can be said that it is preferred to be referred to as 6-50 micrometers by a use.

[0018]If mass production nature is taken into consideration, it is desirable to consider it as a long shape film so that a thin film can be formed continuously.

[0019]The thin film layer 3 consists of a vacuum evaporation film of metallic oxides, such as magnesium oxide, oxidized silicon, and an aluminum oxide, and has transparency, and should just have GASUBARIA nature, such as oxygen and a steam. Especially magnesium oxide especially is excellent in transparency and GASUBARIA nature. However, the thin film layer 3 of this invention can be used if it is the material which suits the above-mentioned conditions, without being limited to the metallic oxide of magnesium oxide, oxidized silicon, and an aluminum oxide.

[0020]the kind and composition of the metallic oxide in which the thickness of the thin film layer 3 is used -- an optimal condition -- things -- it is desirable for **** to be generally within the limits of 300-3000 A, and the value is chosen suitably. However, thickness is not [that the whole surface of the substrate 2 does not become a film about thickness for it to be less than 300A, or] sometimes enough, and the function as a gas barrier material may fully be unable to be achieved. It is because flexibility cannot be made to hold to a thin film, but it bends after membrane formation and there is a possibility of producing a crack in a thin film, according to external factors, such as hauling, when exceeding 3000 A for thickness.

[0021]Although it is variously as a method of forming the thin film layer 3 which consists of metallic oxides on the substrate 2 and can form with the usual vacuum deposition method, sputtering process, the ion plating method, etc. which are other methods for forming thin film can be used. However, if productivity is taken into consideration, at present, the vacuum deposition method is most excellent. It is preferred to make the heating method of the vacuum evaporator by a vacuum deposition method into an electron beam heating method, and in order to raise the adhesion of a thin film and a substrate, and the compactness of a thin film, it is also possible to use the plasma assisting method and ion beam assist method.

[0022]The transparent primer layer 4 is laminated on the thin film layer 3, and can absorb and ease mechanical stress, such as cover printing of the Serra part in hauling contraction, etc. and bag manufacture at the time of printer's ink desiccation, by a transparent primer layer, It is indispensable when especially the metal oxide thin film layer 3 is comparatively as thin as 500-1500 A.

[0023]Although the transparent primer layer 4 is low ductility, and it is preferred that it is a coat of high hardness and a presentation in particular is not limited, it comprises a polymer material which has the transparency which is not less than 60 ** of glass transition points, and has a molecular weight between 10000-20000.

[0024]In glass transition points' [less than 60 ** of] case, since there is no stability in ordinary temperature, by cover printing of the Serra part in hauling contraction, etc. and bag manufacture by desiccation of printer's ink, etc., the coat of the transparent primer layer 4 causes a dimensional change, a crack occurs in the thin film layer 3, and GASUBARIA nature falls. Since the pliability of a coat will fall and the same problem will arise if a glass transition point becomes not much high too much although it does not produce but the above-mentioned problem is good if it is not less than 60 ** of glass transition points, it is preferred preferably that a glass transition point shall be 60-80 **.

[0025]Since, as for less than 10000 thing, a molecular weight becomes small, the molecular weight of resin is low ductility, but. Since relaxation of mechanical stress, such as cover printing [in / elongation becomes large and / hauling, contraction, etc. of printer's ink, and a bag sealer], becomes less enough [what a coat becomes weak and there is a problem on intensity, and exceeds 20000], a molecular weight is between 15000-18000 preferably.

[0026]As primer resin which fulfills the above-mentioned conditions, For example, a polyvinyl chloride

system, a polyvinyl chloride acetate copolymer, a polyvinyl-butyl system, Thermosetting polymer resin, such as thermoplastic polymer resin, such as a polymethyl methacrylic system, a polyurethane system, a polyester system, a polyamide system, a nitrocellulose system, and a cellulosic system, or a melamine system, and a urea system, can be used, and it is suitably chosen from these. A hardening agent etc. can be added if needed and it can also be used as a bridging body. It excels especially in dimensional stability and polyester resin is mentioned as what has a good adhesive property with a substrate and photogravure coating fitness.

[0027]As an organic solvent which dissolves primer resin, Will not be limited especially if it is possible to dissolve resin, and for example, What was blended independently or arbitrarily among aromatic hydrocarbon, such as ketone, such as ester species, such as ethyl acetate and butyl acetate, methyl ethyl ketone, and methyl isobutyl ketone, toluene, and xylene, is used. What mixed toluene and methyl ethyl ketone from the field of coat processing and a bad smell preferably is preferred.

[0028]As a formation method of the transparent primer layer 4, the coating method of well-known of the printing method of well-known of offset printing, gravure, a silk-screen-printing method, etc., a roll coat, a knife-edge coat, gravure coating, etc., etc. can be used, for example.

[0029]If coat formation of the thickness of the transparent primer layer 4 can be carried out uniformly, it will not be limited in particular, but it is preferred to coat 0.2 micrometers or more practical. It is because the thing below 0.2 micrometer cannot perform coat formation with uniform thickness in many cases, relaxation of mechanical stress, such as hauling, contraction, etc. of printer's ink, and cover printing in a bag sealer, becomes less enough [the thing] and there is a possibility that GASUBARIA nature may fall. When thickness exceeds 1.0 micrometer, there is a problem in respect of the bad smell of the solvent etc. which remain in primer resin, and the thickness of the transparent primer layer 4 has the good range of 0.5-1.0 micrometer especially preferably.

[0030]It is also possible to laminate other layers on the transparent primer layer 4. For example, they are a printing layer and a heat seal layer. A printing layer is what is formed in order to use practical as a packed body etc., It is a layer constituted in the ink in which the ink binder resin used from the former, such as a urethane system, acrylic, a nitrocellulose system, a rubber system, and a VCM/PVC system, comes to add various paints, an extender and a plasticizer, a drier, stabilizer, etc., and designs, such as a character and a pattern, are formed. As a formation method, the coating method of well-known of the printing method of well-known of offset printing, gravure, a silk-screen-printing method, etc., a roll coat, a knife-edge coat, gravure coating, etc., etc. can be used, for example. 0.1-2.0 micrometers of thickness may be sufficient.

[0031]A heat seal layer is used for jointing at the time of forming in a saccate packed body etc. Resin, such as polyethylene, polypropylene, an ethylene-vinylacetate copolymer, an ethylene-methacrylic acid copolymer, an ethylene-methacrylic-acid-ester copolymer, an ethylene-acrylic acid copolymer, ethylene-acrylic ester copolymers, and those metal bridge construction things, is used.

Although thickness is determined according to the purpose, generally it is the range of 15-200 micrometers. Heat melting of the method and the above-mentioned resin which laminate the thing of the film state which consists of the above-mentioned resin by the dry laminate method and the non solvent laminating method as a formation method can be carried out, and it can laminate by publicly known methods, such as the EKISUTO Roussillon laminating method extruded and pasted together to curtain form.

[0032]Concrete working example is given and the deposition film layered product of this invention is explained.

[0033][Working example 1] With the vacuum evaporator by the electron beam heating method which is not illustrated as the substrate 2 on one side of the polyethylene terephthalate (PET) film of 12 micrometers of thickness, it vapor-deposited in thickness of about 500 Å, the thin film layer 3 was formed for magnesium oxide, and the magnesium oxide deposition film was obtained. When the vacuum evaporation thickness of the obtained deposition film was measured with X-ray fluorescence analysis, it was 550-600 Å in thickness, and when the oxygen permeability of this film was measured, the value of 2.0-3.0 (cc/m²/day) was shown.

[0034]Subsequently, this magnesium oxide deposition film was coated by the following resin primers, and the transparent resin primer layer 4 was formed.

- Resin : Polyester glass transition point : 67 ** and molecular weight : 18000 and thickness : 0.70 micrometer

[0035]Furthermore urethane system printer's ink 4 color (sumi, red, yellow, white) was used for the transparent resin primer layer 4, gravure printing was performed, and the layered product was obtained.

[Working example 2] To the outermost layer of the layered product of working example 1, polypropylene (CCP) 30micrometer was laminated by the dry laminate method.

[0036][Working example 3] To the outermost layer of working example 1 and a layered product, 15 micrometers was laminated for polyethylene (PE) by the EKISUTO Roussillon laminating method.

[0037][Comparative example 1] The transparent primer layer 4 was not formed in the deposition film for the resin primer of working example 1, but gravure printing was performed using direct urethane system printer's ink 4 color (sumi, red, yellow, white), and the layered product was obtained.

[0038][Working example 4] The resin primer of working example 1 was changed into the following composition, and the layered product was similarly obtained except it.

- Resin : Polyester glass transition point : 67 ** and molecular weight : 18000 and thickness : 0.28 micrometer [0039][Comparative example 2] The resin primer of working example 1 was changed into the following composition, and the layered product was similarly obtained except it.

- Resin : Polyester glass transition point : 60 ** and molecular weight : 2000 and thickness : 0.75 micrometer [0040][Comparative example 3] The resin primer of working example 1 was changed into the following composition, and the layered product was similarly obtained except it.

- Resin : Polyester glass transition point : 7 ** and molecular weight : 20000 and thickness : 0.84 micrometer [0041][Working example 5] The resin primer of working example 1 was changed into the following composition, and the layered product was similarly obtained except it.

- Resin : Polyurethane glass transition point : 70 ** and molecular weight : 15000 and thickness : 1.03 micrometers [0042][Comparative example 4] The resin primer of working example 1 was changed into the following composition, and the layered product was similarly obtained except it.

- Resin : Polyurethane glass transition point : 47 ** and molecular weight : 25000 and thickness : 1.10 micrometers [0043][Working example 6] The resin primer of working example 1 was changed into the following composition, and the layered product was similarly obtained except it.

- Resin : Nitrocellulose glass transition point : 80 ** and molecular weight : 20000 and thickness : 0.69 micrometer [0044][Working example 7] Polo propylene 30micrometer was laminated to the layered product of working example 1 which is not printing by the dry laminate method, and it was processed into it with the bag sealer.

[0045][Comparative example 5] Polo propylene 30micrometer was laminated to the layered product of the comparative example 1 which is not printing by the dry laminate method, and it was processed into it with the bag sealer.

[0046][Working example 8] With the vacuum evaporator by the electron beam heating method which is not illustrated as the substrate 2 on one side of the polyethylene terephthalate (PET) film of 12 micrometers of thickness, it vapor-deposited in thickness of about 400 Å, the thin film layer 3 was formed for oxidized silicon, and the oxidized silicon deposition film was obtained. When the oxygen permeability of the obtained deposition film was measured, the value of 2.0-3.0 (cc/m²/day) was shown.

[0047]Subsequently, the following resin primers were coated for this oxidized silicon deposition film by the gravure coating method, and the transparent resin primer layer 4 was formed.

- Resin : Polyester glass transition point : 67 ** and molecular weight : 18000 and thickness : 0.70 micrometer [0048]Furthermore, polypropylene (CCP) 30micrometer was laminated to the outermost layer of this layered product by the dry laminate method, and it was processed with the bag sealer.

[0049][Comparative example 6] The resin primer of working example 8 was changed into the following composition, and except it, it laminated similarly and was processed with the bag sealer.

- Resin : Polyester glass transition point : 7 ** and molecular weight : 20000 and thickness : 0.80 micrometer [0050][Comparative example 7] The transparent primer layer 4 was not formed in the deposition film of working example 8, but polypropylene 30micrometer was laminated by the dry laminate method, and it was processed with the bag sealer.

[0051]Measurement of the oxygen permeability (cc/m²/day) before and behind the printing stratification of each layered product and after heat seal layer lamination and bag-making processing and the evaluated result were indicated to Table 1 above.

[0052]

[Table 1]

△	蒸着物	プライマー層 樹脂組成	熱転移点 (°C)	分子量	厚さ (μ)	t-トシル酸 格指 μ	酸素透過率 (cc/m ² /day)				評価
							印刷前	印刷後	横層後	製袋後	
実施例1	MgO	剤1&剤2	67	18000	0.70	—	2.63	1.98	—	—	◎
実施例2	MgO	剤1&剤2	67	18000	0.70	CCP 30	2.63	1.98	1.67	—	◎
実施例3	MgO	剤1&剤2	67	18000	0.70	PB 15	2.63	1.98	1.88	—	◎
比較例1	MgO	—	—	—	—	—	2.63	15.77	—	—	×
実施例4	MgO	剤1&剤2	67	18000	0.28	—	2.63	3.56	—	—	○
比較例2	MgO	剤1&剤2	60	2000	0.75	—	2.63	均一塗布困難			×
比較例3	MgO	剤1&剤2	70	20000	0.84	—	2.63	12.32	—	—	×
実施例5	MgO	剤1&剤2	70	15000	1.03	—	2.63	3.38	—	—	○
比較例4	MgO	剤1&剤2	47	25000	1.10	—	2.63	16.68	—	—	×
実施例6	MgO	ニトロアーバス	80	20000	0.69	—	2.63	2.91	—	—	○
実施例7	MgO	剤1&剤2	67	18000	0.70	CCP 30	2.47	—	1.86	1.81	◎
比較例5	MgO	—	—	—	—	CCP 30	2.72	—	2.91	11.31	×
実施例8	SiO	剤1&剤2	67	18000	0.70	CCP 30	2.51	—	1.89	2.00	◎
比較例6	SiO	剤1&剤2	7	20000	0.80	CCP 30	2.55	—	1.60	4.10	×
比較例7	SiO	—	—	—	—	CCP 30	2.34	—	2.00	6.45	×

[0053]. Made the comparative example into the conditions used as the above-mentioned packed body to working example. High gas-barrier ** which intercepts the transparency which can face the contents themselves squarely, the gas which affects it to contents, etc. It can say that it is not what fills all the mechanical strengths (or flexibility) to which a function is not reduced to the physical and mechanical stress by processing to a packed body, etc.

[0054]

[Effect of the Invention] In [as stated above, according to this invention excel in the transparency after membrane formation, and GASUBARIA nature, and] the process of post processing, As opposed to an operation of bending and hauling from the outside by contraction and the bag sealer of printer's ink, cover printing, etc., The transparency which is the conditions which do not produce the damage to a film crack etc. in a thin film, and are used as the above-mentioned packed body, It has a gas-barrier ** mechanical strength and flexibility nature, and while maintaining the transparency which a metal oxide thin film has, and GASUBARIA nature originally, the layered product which can fully demonstrate practicality is obtained.

[Translation done.]